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(54) Title: METHOD OF PRODUCING SILVER-COPPER ALLOYS

(57) Abstract: A method of producing a ternary alloy of silver, copper and germanium, or a quaternary alloy of silver, copper, zinc and germanium, is provided, comprising casting a molten mixture of silver, copper, germanium, and optionally zinc, to form a solidified alloy, and processing and annealing the sheet to reduce its thickness and re-crystallise grains in the alloy. The annealing is carried out under a selectively oxidising atmosphere, preferably an atmosphere comprising nitrogen, hydrogen and moisture, to afford firestain resistance and improved tarnish resistance to the alloy.

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## METHOD OF PRODUCING SILVER-COPPER ALLOYS

### 5 TECHNICAL FIELD

This invention relates to a method for the production of silver-copper alloys, in particular silver-copper-germanium ternary alloys and silver-copper-zinc-germanium quaternary alloys, that exhibit firestain resistance and improved tarnish resistance.

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### BACKGROUND ART

Silver-based alloys containing copper are well known and commonly used in the fields of jewellery, silver holloware, electronics and dentistry. Because of the soft and ductile  
15 nature of silver, copper is included in the alloy to provide a satisfactory hardness to the material, whilst retaining the lustre and malleability of the silver. The relative amounts of silver and copper contained in the alloy may be selected as appropriate to the desired end use or application. For jewellery purposes, for example, silver alloys commonly contain a minimum of either 92.5% or 80% silver, by weight, according to first and second silver  
20 standards in force in continental Europe, with the remainder being copper. For example, Sterling silver comprises at least 92.5% silver, the remainder copper. Lesser silver contents may be used in alloys for dentistry purposes, or as solder/brazing material, or for electronics applications.

25 Silver-copper-germanium alloys can be produced by casting a molten mixture of the alloy metals into a static mould, or by continuous casting, and allowing the metal to cool and solidify to form an ingot or strip of solidified cast alloy. The surface of the cast alloy may be stripped off or scalped to remove the copper-rich chill cast layer. The cast alloy can then be processed, by rolling, drawing, extruding or forging, to sheet, rod, wire or tube.  
30 For example, the alloy may be cold-rolled using compression rollers, so as to reduce the thickness of the ingot and thereby also reduce the grain size microstructure of the alloy.

The alloy is annealed by treating the processed alloy in a furnace at a suitable annealing temperature to re-crystallise the grain structure in the alloy. The processing and annealing steps are usually repeated, as often as necessary, according to well known practice in the art. The processing and annealing thus converts the coarse, cast structure of the alloy into a thinner, more homogeneous, finer grained, workable alloy.

A well known problem associated with silver-copper alloys is the tendency of the copper to oxidise, particularly at high temperatures such as those used during the casting and processing of the alloy. The cuprous or cupric oxides give rise to so-called firestaining, whereby dark stains appear in the alloy metal surface during casting, annealing, soldering, brazing and/or re-casting. Therefore, annealing is conventionally carried out under a dry reducing atmosphere in order to prevent, as far as possible, the formation of copper oxides which cause firestaining.

Silver, on the other hand, does not readily oxidise at high or even ambient temperatures, but tarnishes easily by reacting with sulphur or hydrogen sulphide.

It is known that both firestaining and tarnishing in silver-copper alloys can be mitigated by the inclusion of small amounts of germanium in the alloy. Germanium has a greater affinity for oxygen than silver or copper and forms a very thin coating of germanium oxide, generally represented as  $\text{GeO}_x$  (wherein  $x=1$  or  $2$ ), in the ternary silver-copper-germanium alloy. This oxide layer, which is transparent and invisible to the naked eye, fulfils a protective role and thus further prevents the formation of copper oxides (firestaining) during annealing of the alloy. Germanium also sulphurises preferentially compared with silver and thus reduces the tendency of the alloy to tarnish during and after processing. Thus, germanium oxide and possibly germanium sulphide form at the surface, or as discrete precipitates mainly below the surface, of the alloy.

The measure of using a dry reducing atmosphere in the production of the alloy and the recognition that germanium has the ability to form a protective germanium oxide coating has allowed ternary silver-copper-germanium alloys to be produced that exhibit good firestain resistance when further annealed in air. However, poor tarnish resistance may

still be observed in practice in these ternary alloys despite the inclusion of germanium in the alloy composition.

We have now found, surprisingly, that it is possible to eliminate, or at least consistently  
5 reduce the likelihood or rate of tarnishing in silver-copper-germanium ternary alloys and in silver-copper-zinc-germanium quaternary alloys, whilst retaining good firestain resistance. Moreover, we have found that it is possible to achieve this goal by measures that do not require additional processing steps or costly alteration of existing production means. This has been achieved by using a controlled gaseous atmosphere during the production of the  
10 alloy, instead of the dry reducing atmosphere that was previously assumed to be essential to prevent the formation of copper oxides.

#### SUMMARY OF THE INVENTION

15 Accordingly, in one aspect the present invention provides a method of producing an alloy of silver, copper and germanium, and optionally zinc, which comprises casting a molten mixture of silver, copper and germanium, and optionally zinc (and preferably a grain refiner) to form a solidified alloy, and processing and annealing the alloy to reduce its thickness and re-crystallise grains in the alloy, wherein the annealing is carried out under a  
20 selectively oxidising atmosphere, preferably a wet selectively oxidising atmosphere, to afford firestain resistance and improved tarnish resistance to the alloy.

In other aspects, the invention provides alloys produced by the method above, and finished  
25 and semi-finished articles produced from the alloy.

#### DISCLOSURE OF THE INVENTION

At the moderately high temperatures used to produce the alloy, the controlled gaseous atmosphere modifies the surface properties of the solid silver alloy by selectively oxidising  
30 the germanium constituent present in the alloy. As a result, the alloy thus produced demonstrates an increased resistance to tarnishing reactions, as compared with alloys of the same ternary or quaternary composition produced under a conventional dry reducing

atmosphere. It is believed that the controlled furnace atmosphere, for example a furnace atmosphere containing gases including nitrogen and hydrogen with a controlled amount of water vapour, provides an oxidising environment which creates the desired protective oxides, whereas a conventional dry furnace atmosphere containing hydrogen may reduce any oxides back to metal during production.

It should be appreciated that the oxidation of alloys is complex, and dependent on a number of influencing factors. Thus, different alloys show different types of oxidation behaviour depending mainly on the specific metals of which the alloy is composed and the relative amounts of these metals present in the alloy, *i.e.* the composition, the nature and stabilities of the oxides that the metals can form, the interaction, if any, between these oxides, and the oxidising conditions concerned, such as the gas composition, the temperature and gas partial pressures. It is found, for example, that with Ag-Cu alloys, *e.g.* Sterling silver, it is the Cu which is oxidised to form  $\text{Cu}_2\text{O}$  and/or  $\text{CuO}$  whereas with Fe-Cu alloys it is the Fe which is oxidised. The question as to which component will preferentially oxidise in a given alloy is governed by thermodynamic factors. The rate at which the oxide forms is governed by kinetic factors.

To understand this further, alloys can be broadly classified into two types:

(a) noble parent metal with base alloying elements

*e.g.* Au, Ag, or Pt, which do not form stable oxides under normal conditions, alloyed with elements such as Cu, Ni, Fe, Co, Cr, Al, Ti, and In, which do form stable oxides. However, at reduced oxygen pressures, metals such as Cu, Ni and Co, which form oxides of moderate stability, can behave as noble parent metals; and

(b) base parent metal with base alloying elements

*e.g.* Cu, Ni, Fe alloyed with Cr, Si, Co.

The ternary and quaternary alloys produced according to the present invention, namely Ag-Cu-Ge alloys and Ag-Cu-Zn-Ge alloys, are of type (a) and include two base metal alloying

elements, Cu and Ge, in a noble parent metal, Ag. On exposure to an oxidising atmosphere, two oxidation reactions have to be considered.

Firstly, the oxidation of copper to cuprous oxide:

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Secondly, the oxidation of germanium to germanium (di)oxide:

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Under standard state conditions, *i.e.* for pure Cu and pure Ge each reacting with pure oxygen gas at 1 atm pressure to form the pure oxide phase, both reactions are feasible, with the chemical driving force for reaction (2) being higher than that of reaction (1) by a factor of 1.65.

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Table 1 demonstrates the theoretical minimum oxygen potential required to oxidise each of pure Ge, pure Cu and pure Ag to its corresponding oxide, at 625°C and 650°C, as calculated from the Standard Gibbs Energy of Reaction for each oxidation reaction. Table 1 further shows the minimum dew points that would be needed for an H<sub>2</sub>O/H<sub>2</sub> atmosphere at 625°C and 650°C to be able to oxidise each of pure Ge, pure Cu and pure Ag to its corresponding oxide, and indicates that, in principle, it is possible to formulate an H<sub>2</sub>/H<sub>2</sub>O atmosphere having a dew point such that pure Ge would be oxidised without pure Cu being oxidised, for example an H<sub>2</sub>/H<sub>2</sub>O atmosphere having a dew point of 87°C to 95°C:

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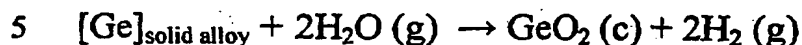
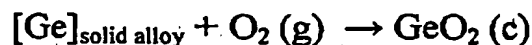
Table 1:

Oxidation Reaction	Temperature (°C)	Standard Gibbs Energy of Reaction per mole O <sub>2</sub> (g) (Jmol <sup>-1</sup> )	Equilibrium Oxygen Potential PO <sub>2</sub> (atm)	Equilibrium (PH <sub>2</sub> O/PH <sub>2</sub> ) ratio	Dew Point of H <sub>2</sub> O/H <sub>2</sub> mixture (°C)
Ge(s)+O <sub>2</sub> (g) → GeO <sub>2</sub> (s)	625	-3.918 x 10 <sup>5</sup>	1.613 x 10 <sup>-23</sup>	1.37	85.12
	650	-3.879 x 10 <sup>5</sup>	1.118 x 10 <sup>-22</sup>	1.47	86.66
4Cu(s)+O <sub>2</sub> (g) → 2Cu <sub>2</sub> O(s)	625	-2.058 x 10 <sup>5</sup>	1.066 x 10 <sup>-12</sup>	3.52 x 10 <sup>5</sup>	~100
	650	-2.0216 x 10 <sup>5</sup>	3.620 x 10 <sup>-12</sup>	2.64 x 10 <sup>5</sup>	~100
4Ag(s)+O <sub>2</sub> (g) → 2Ag <sub>2</sub> O(s)	625	+5.195 x 10 <sup>4</sup>	1.052 x 10 <sup>3</sup>	1.104 x 10 <sup>13</sup>	~100
	650	+5.4755 x 10 <sup>4</sup>	1.256 x 10 <sup>3</sup>	4.92 x 10 <sup>12</sup>	~100

However, in the present Ag-Cu-(Zn)-Ge alloys, there is a significant difference between the Cu and the Ge contents, *e.g.* Sterling silver 92.5% Ag material typically contains 6.5 % Cu and 1% Ge by weight. This results in a larger difference between the thermodynamic activities of Cu and Ge in the ternary alloy which reduces the difference in the driving forces considerably.

- 10 We have found that it is possible to have mildly oxidising conditions, *i.e.* temperatures and oxygen partial pressures, which allow the Ag-Cu-(Zn)-Ge alloys to be processed such that Ge will react to form GeO<sub>2</sub> without Cu forming Cu<sub>2</sub>O. However, restrictions on the maximum processing temperature and time at temperature arise from the normal commercial annealing temperature and time used for producing silver-copper alloys such as Sterling silver, typically about 625°C or 650°C. We have established that the Ag-Cu-(Zn)-Ge alloys can be processed even at annealing temperatures such as 625°C and 650°C to selectively oxidise Ge to GeO<sub>2</sub>, by using a controlled atmosphere such that the range of oxygen potential provided by the atmosphere at temperature forms GeO<sub>2</sub> whilst preventing the formation of Cu<sub>2</sub>O. We found that these requirements could be satisfied by an atmosphere of, for example, H<sub>2</sub>/H<sub>2</sub>O or CO/CO<sub>2</sub>.

Table 2 demonstrates the theoretical minimum oxygen potentials required to oxidise Ge in each of two Ag-Cu-Ge alloys, at 625°C and 650°C, by the oxidation reaction:



The data in Table 2 further shows the minimum water : hydrogen ratios required to achieve the minimum oxygen potentials, and the corresponding minimum dew points that would be needed for an H<sub>2</sub>/H<sub>2</sub>O atmosphere. The dew points may be derived from the equation for vapour pressure of water from freezing point to boiling point:

10

$$\log_{10} P_{\text{H}_2\text{O}} (\text{mm Hg}) = -(2900/T) - 4.65\log_{10}(T) + 22.613$$

(see "Metallurgical Thermochemistry", O.Kubaschewski & C.B.Alcock (Pergamon Press), 5<sup>th</sup> Edition (1979), page 362).

15

Thus, by using an H<sub>2</sub>/H<sub>2</sub>O atmosphere having a dew point at or above the minimum dew point, we showed that it is possible to selectively oxidise Ge in the alloys:

Table 2:

20

Alloy composition (by weight)	Temperature (°C)	Oxygen Potential PO <sub>2</sub> minimum value for GeO <sub>2</sub> formation (atm)	(PH <sub>2</sub> O/PH <sub>2</sub> ) ratio required to give minimum PO <sub>2</sub>	Partial Pressure of H <sub>2</sub> O(g) at 1 atm total (atm) ((mm Hg))	Dew Point of H <sub>2</sub> O/H <sub>2</sub> mixture (°C)
92.5 % Ag 6.4 % Cu 1.1 % Ge	625	6.147 x 10 <sup>-22</sup>	0.1185	0.1059 (80.48)	47.20
	650	4.040 x 10 <sup>-22</sup>	0.1133	0.1018 (77.37)	46.44
80.0 % Ag 18.5 % Cu 1.5 % Ge	625	6.306 x 10 <sup>-21</sup>	0.0369	0.03566 (27.10)	27.23
	650	3.889 x 10 <sup>-20</sup>	0.0365	0.03524 (26.78)	27.03



Moreover, we were able to show experimentally that the Ge oxidation reaction proceeds at a sufficiently high rate in practice to form  $\text{GeO}_2$  of a sufficient thickness during the times at temperature normally used in Ag-alloy annealing. X-ray diffraction measurements on Ag-Cu-Ge samples following oxidation under a controlled oxygen potential showed that  $\text{GeO}_x$  is indeed formed in detectable amounts. Finally, we have shown that the  $\text{GeO}_2$  film produced under the controlled atmosphere is effective to enhance the tarnish resistance of the alloy.

According to the present invention, the annealing is carried out under a selectively oxidising atmosphere. By 'selectively oxidising' in this context is meant an atmosphere having an oxygen potential such that germanium is oxidised to germanium oxide ( $\text{GeO}_x$  wherein  $x=1$  or  $2$ ) without oxidising copper to copper oxides that would cause any significant firestaining.

The atmosphere comprises at least one non-oxidising gas, which may be an inert gas such as argon or nitrogen, or, preferably, a reducing gas such as hydrogen, dissociated ammonia or carbon monoxide. Accordingly, suitable non-oxidising gases include hydrogen, dissociated ammonia, carbon monoxide, nitrogen, argon, or mixtures thereof. In addition, the atmosphere comprises at least one oxidising gas such as  $\text{H}_2\text{O}$  (steam), oxygen or carbon dioxide. The proportions of non-oxidising and oxidising gases will be chosen to provide an oxygen potential, at the annealing temperature used, such that germanium is selectively oxidised to germanium oxide. Suitably, the selectively oxidising atmosphere comprises hydrogen and  $\text{H}_2\text{O}$ , or carbon monoxide and carbon dioxide, or is of argon or nitrogen and oxygen.

For example, in one embodiment, the selectively oxidising atmosphere is provided by an inert gas such as, but not limited to, argon or nitrogen, to which a controlled amount of oxygen has been added. Typically, the oxygen is added so as to provide an atmosphere having an oxygen content of from 0.1 to 0.5 % by volume.

- Preferably, the atmosphere is a wet selectively oxidising atmosphere. By 'wet' in this context is meant an atmosphere containing moisture ( $H_2O$ ), such that the atmosphere exhibits a dew point of at least  $+1^{\circ}C$ , preferably at least  $+25^{\circ}C$ , more preferably at least  $+40^{\circ}C$ . Preferably, the dew point falls within the range from  $+1^{\circ}C$  to  $+80^{\circ}C$ , more preferably in the range from  $+2^{\circ}C$  to  $+50^{\circ}C$ . The dew point may be defined as the temperature to which an atmosphere containing water vapour must be cooled in order for saturation to occur, whereby further cooling below the dew point temperature results in the formation of dew. A more comprehensive definition is given in "Handbook of Chemistry and Physics", 65<sup>th</sup> Edition (1985-85), CRC Press Inc., USA, page F-75. We prefer that the selectively oxidising atmosphere comprises hydrogen and moisture, for example an atmosphere of nitrogen, hydrogen and water vapour, such as a 95% nitrogen / 5% hydrogen gas mixture (v/v) containing water vapour, or a furnace atmosphere of nitrogen, hydrogen, carbon monoxide, carbon dioxide, methane, and water vapour.
- In practice, it is preferred to produce the wet selectively oxidising atmosphere by controlling the addition of water vapour to a substantially dry inert or dry reducing furnace atmosphere, for example to a furnace atmosphere of predominantly nitrogen or nitrogen and hydrogen, and typically comprising nitrogen, hydrogen, carbon monoxide, carbon dioxide and methane. The dew point in the furnace can be measured by conventional means such as a dew point meter or probe in the furnace, and the gas mixing ratios adjusted accordingly in order to control the selectively oxidising atmosphere.

The annealing of the alloy should be carried out under the selectively oxidising atmosphere. If, as is usual, the annealing is carried out as successive annealing steps, for example with intervening rolling steps, then at least the final annealing step should be carried out under the selectively oxidising atmosphere. If desired, one or more of the annealing steps preceding the final annealing step could be conducted under a reducing atmosphere. However, we prefer that all of the annealing steps are carried out under a selectively oxidising atmosphere.

The annealing is carried out at a temperature in the range from  $400^{\circ}C$  to  $750^{\circ}C$ , typically in the range from  $400^{\circ}C$  to  $700^{\circ}C$ , preferably in the range from  $500^{\circ}C$  to  $675^{\circ}C$ , more

preferably in the range from 600°C to 650°C, and in particular at about 625°C. The annealing is suitably carried out for a total period in the range of from 5 minutes, at the higher annealing temperatures, to 5 hours, at the lower annealing temperatures, and preferably in the range from 15 minutes to 2 hours.

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The solidified alloy is processed to reduce its thickness by any suitably method, such as by rolling, drawing, extruding or forging. Thus, the alloy may be converted into a thinner form such as a sheet, rod, wire or tube. The solidified alloy is processed preferably by rolling, more preferably by cold-rolling, as is known in the art. The rolling and annealing steps may be repeated, if necessary, until the desired final thickness and grain structure has been achieved.

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The ternary Ag-Cu-Ge alloys and quaternary Ag-Cu-Zn-Ge alloys that can suitably be prepared by the method of the present invention are those having a silver content of at least 30%, preferably at least 60%, more preferably at least 80%, and most preferably at least 92.5%, by weight of the alloy, up to a maximum of no more than 98%, preferably no more than 97%.

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The germanium content of the Ag-Cu-(Zn)-Ge alloys should be at least 0.1%, preferably at least 0.5%, more preferably at least 1.1%, and most preferably at least 1.5%, by weight of the alloy, up to a maximum of preferably no more than 6.5%, more preferably no more than 4%.

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If desired, the germanium content may be substituted, in part, by one or more elements which have an oxidation potential selected from Al, Ba, Be, Cd, Co, Cr, Er, Ga, In, Mg, Mn, Ni, Pb, Pd, Pt, Si, Sn, Ti, V, Y, Yb and Zr, provided the effect of germanium in terms of providing firestain and tarnish resistance is not unduly adversely affected. The weight ratio of germanium to substitutable elements may range from 100:0 to 60:40, preferably from 100:0 to 80:20. Preferably, the germanium content consist entirely of germanium, i.e. the weight ratio is 100:0.

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The remainder of the ternary Ag-Cu-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper, which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy. For an '800 grade' ternary alloy, for example, a copper content of 18.5% is suitable. The remainder of the quaternary Ag-Cu-Zn-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy, and zinc which should be present in a ratio, by weight, to the copper of no more than 1 : 1. Therefore, zinc is optionally present in the silver-copper alloys in an amount of from 0 to 100 % by weight of the copper content. For an '800 grade' quaternary alloy, for example, a copper content of 10.5% and zinc content of 8% is suitable.

In addition to silver, copper and germanium, and optionally zinc, the alloys of the invention preferably contain a grain refiner to inhibit grain growth during processing of the alloy. Suitable grain refiners include boron, iridium, iron and nickel, with boron being particularly preferred. The grain refiner, preferably boron, may be present in the Ag-Cu-(Zn)-Ge alloys in the range from 1 ppm to 100 ppm, preferably from 2 ppm to 50 ppm, more preferably from 4 ppm to 20 ppm, by weight of the alloy.

In a preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and any grain refiner, of 80% to 96% silver, 0.1% to 5% germanium and 1% to 19.9% copper, by weight of the alloy.

In a more preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 98% silver, 0.3% to 3% germanium and 1% to 7.2% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.

In a further preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 96% silver, 0.5% to 2% germanium, and 1% to 7% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.

As mentioned, it is believed that the presence of the controlled, mildly oxidising atmosphere, such as provided by moisture in a hydrogen-containing atmosphere, during the production of the ternary or quaternary alloy leads to the preferential formation of germanium oxide in the surface of the alloy or as discrete precipitates mainly below the surface. As a result of processing and annealing the alloy, preferably repeatedly, the germanium oxide becomes concentrated at the grain boundaries and extends into the surface of the alloy, and can thus protect the copper from oxidation and consequent firestaining. Also, tests have shown that it is germanium oxide or dioxide that prevents the formation of silver sulphides. Thus, a silver-copper-germanium ternary alloy or a silver-copper-zinc-germanium quaternary alloy having excellent firestain resistance and tarnish resistance can be realised using the method according to the present invention.

A further improvement in tarnish resistance may be obtained by heating the alloy post-production, *i.e.* after the alloy has been processed and annealed to provide a finished or semi-finished article, and optionally after further suitable treatment and/or finishing, in an air or steam atmosphere at a temperature in the range from 40°C to 220°C, preferably in the range from 50°C to 200°C, more preferably in the range from 60°C to 180°C. Preferably, the post-production heat treatment is carried out for a period in the range from 1 minute to 24 hours, preferably in the range from 10 minutes to 4 hours. Thus, the germanium oxide protective coating may be further developed within the surface of the alloy. Advantageously, this post-production treatment further enhances the alloy protection against tarnishing.

#### BRIEF DESCRIPTION OF FIGURES

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Figure 1 shows a photograph of samples of: (a) 925 Ag-Cu-Ge silver alloy according to the invention, after 3 minutes exposure to H<sub>2</sub>S; (b) 925 Ag-Cu Sterling silver after 1 minute exposure to H<sub>2</sub>S; (c) SP-925 Ag-Cu silver plated Sterling silver after 3 minutes exposure to H<sub>2</sub>S;

30 Figure 2 shows a photograph of a sample of 925 Ag-Cu-Ge silver alloy according to the invention after 5 minutes exposure to H<sub>2</sub>S;

Figure 3 shows a photograph of a sample of 925 Ag-Cu-Ge silver alloy according to the invention after 3 minutes exposure to  $H_2S$ ; and

Figure 4 shows a photograph of samples of (a) 830 Ag-Cu silver plated silver alloy; and (b) 830 Ag-Cu-Ge silver alloy according to the invention, each after one week exposure to flowers of sulphur and calcium nitrate for one week at  $35^\circ C$ .

#### EXAMPLES:

The present invention will be further understood from the following non-limiting examples:

##### Example 1 (Production of alloys):

Ternary Ag-Cu-Ge alloys were prepared (Alloys 1 to 4), as follows:

##### Alloy 1

A ternary silver-copper-germanium alloy (Ag = 92.7%, Ge = 1.1%, B = 4ppm, Cu = Balance) was produced as follows:

A molten mixture of the base metals was cast at a temperature of  $1100^\circ C$  under an atmosphere of nitrogen and was continuously cast to form a cast ingot of 11 mm thickness. A layer of 0.1 mm thickness was scalped off of the surface of the cast ingot by a metal planer.

The cast ingot was cold-rolled in air and reduced in thickness by 40%.

The alloy was annealed in a furnace for 20 minutes at  $630^\circ C$  under a hydrogen gas atmosphere containing moisture. The furnace dew point was  $+25^\circ C$ .

The annealed alloy was then cooled before being cold-rolled to a final thickness of 1 mm.

The alloy was annealed again for 20 minutes at  $630^\circ C$  under a hydrogen gas atmosphere containing moisture. The furnace dew point was  $+25^\circ C$ .

The resulting alloy material is referred to as '925 Ag-Cu-Ge (Alloy 1)'.

#### **Alloy 2**

- 5 A ternary silver-copper-germanium alloy (Ag = 92.7%, Ge = 1.08%, B = 4ppm, Cu = Balance) was produced in the same manner and under the same conditions as described above for Alloy 1, except that the furnace dew point in both the annealing steps was +75°C.

- 10 The resulting alloy material is referred to as '925 Ag-Cu-Ge (Alloy 2)'.

#### **Alloy 3 (comparative)**

- A ternary silver-copper-germanium alloy (Ag = 92.7%, Ge = 1.1%, B = 4ppm, Cu = Balance) was produced in the same manner and under the same conditions as described above for Alloy 1, except that the furnace atmosphere in the annealing steps was a dry hydrogen gas atmosphere having a negative °C furnace dew point.
- 15

The resulting alloy material is referred to as '925 Ag-Cu-Ge (Alloy 3)'.

#### **Alloy 4**

- 20 A ternary silver-copper-germanium alloy (Ag = 83.3%, Ge = 1.5%, B = 6ppm, Cu = Balance) was produced in the same manner and under the same conditions as described above for Alloy 1, except that a different alloy composition was used.

- 25 The resulting alloy material is referred to as '830 Ag-Cu-Ge (Alloy 4)'.

#### **Examples 2 to 4 (Tarnish trials):**

Tarnish trials were performed using the ternary Ag-Cu-Ge materials of Alloys 1, 2, 3 and 4:

#### **Example 2 (Tarnish trial 1)**

30 Samples of 925 Ag-Cu-Ge (Alloy 1), Sterling silver (925 Ag-Cu) and silver plated Sterling silver (SP-925 Ag-Cu) were exposed to hydrogen sulphide gas by suspending the samples

30 mm above an open beaker of 20% ammonium sulphate solution, which decomposes in air to produce hydrogen sulphide gas. The samples were suspended above the solution to expose them to the fume for the times stated, and visually assessed for evidence of tarnishing, as shown in Figures 1(a)-(c) and reported in the results below:

5

**Results:**

925 Ag-Cu-Ge (Alloy 1)	-	3 minute exposure	-	Slight yellowing
925 Ag-Cu	-	1 minute exposure	-	Heavily tarnished
SP-925 Ag-Cu	-	3 minute exposure	-	Heavily tarnished

10

**Example 3 (Tarnish trial 2)**

Sample of 925 Ag-Cu-Ge (Alloy 2) and 925 Ag-Cu-Ge (Alloy 3) were exposed to hydrogen sulphide gas as described in Tarnish trial 1, for 5 minutes, and visually assessed for evidence of tarnishing, as shown in Figure 2 (Alloy 2) and Figure 3 (Alloy 3) and reported in the results below:

15

**Results:**

925 Ag-Cu-Ge (Alloy 2)	-	5 minute exposure	-	Starting to yellow
925 Ag-Cu-Ge (Alloy 3)	-	3 minute exposure	-	Heavily tarnished

20

**Example 4 (Tarnish trial 3)**

Samples of 830 Ag-Cu-Ge (Alloy 4) and silver plated 83%/17% silver-copper alloy (SP-830 Ag-Cu) were placed in a desiccator and exposed to flowers of sulphur and calcium nitrate for one week at 35°C. The exposed samples were visually assessed for evidence of tarnishing, as shown in Figures 4 (a) and (b) and reported in the results below:

25

**Results:**

830 Ag-Cu-Ge (Alloy 4)	-	one week exposure	-	Slight yellowing
SP-830 Ag-Cu	-	one week exposure	-	Heavily tarnished

30



From the results of Tarnish trials 1 to 3 above, it may be seen that Alloys 1,2 and 4 produced according to the method of the present invention showed superior tarnish resistance compared with comparative alloys such as Alloy 3.

**CLAIMS:**

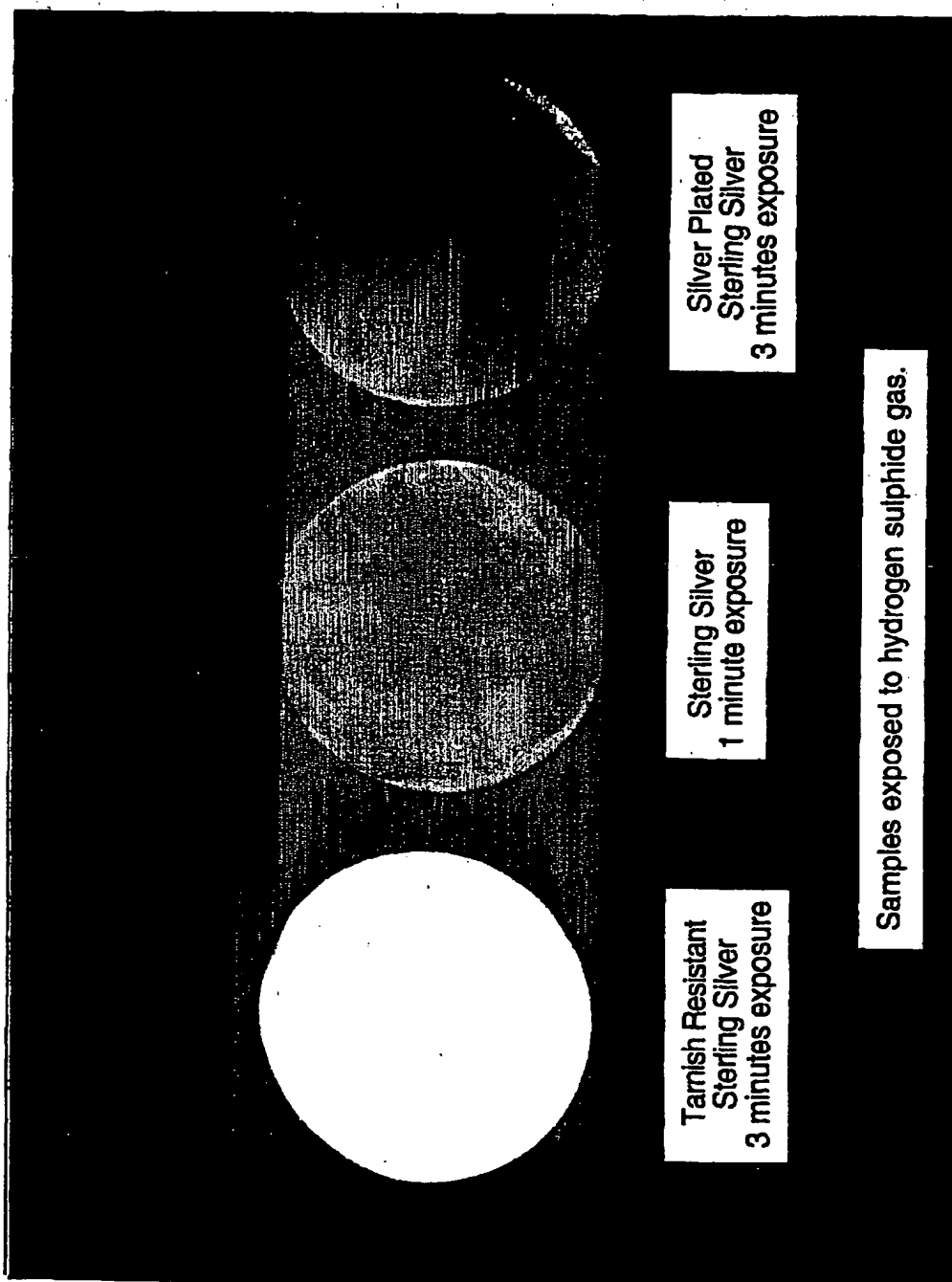
1. A method of producing an alloy of silver, copper and germanium, and optionally zinc, which comprises casting a molten mixture of silver, copper and germanium, and  
5 optionally zinc, to form a solidified alloy, and processing and annealing the alloy to reduce its thickness and re-crystallise grains in the alloy, characterised in that the annealing is carried out under a selectively oxidising atmosphere to afford firestain resistance and improved tarnish resistance to the alloy.
- 10 2. A method according to claim 1 wherein the selectively oxidising atmosphere is a wet selectively oxidising atmosphere.
3. A method according to claim 2 wherein the wet selectively oxidising atmosphere comprises hydrogen gas and moisture.  
15
4. A method according to claim 1 wherein the selectively oxidising atmosphere comprises carbon monoxide and carbon dioxide.
5. A method according to any preceding claim wherein the selectively oxidising  
20 atmosphere comprises nitrogen, hydrogen, carbon monoxide, carbon dioxide, methane, and moisture.
6. A method according to claim 1 wherein the selectively oxidising atmosphere is of argon or nitrogen, and oxygen.  
25
7. A method according to any preceding claim, wherein the atmosphere has a dew point of at least +1°C.
8. A method according to claim 7, wherein the atmosphere has a dew point in the  
30 range from +1°C to +80°C.

9. A method according to claim 8, wherein the atmosphere has a dew point in the range from +2°C to +50°C.
10. A method according to any preceding claim, wherein the alloy is processed to reduce its thickness by rolling the solidified alloy to form a sheet of the alloy.
11. A method according to claim 10, wherein the solidified alloy is cold-rolled.
12. A method according to any preceding claim, wherein the annealing is carried out at a temperature in the range from 400°C to 700°C.
13. A method according to claim 12, wherein the annealing is carried out at a temperature in the range from 500°C to 675°C for a total period in the range of from 5 minutes to 5 hours.
14. A method according to claim 13, wherein the annealing is carried out at a temperature in the range from 600°C to 650°C for a total period in the range of from 15 minutes to 2 hours.
15. A method according to any preceding claim, wherein the annealing comprises a plurality of successive annealing steps, and the final annealing step is carried out under the selectively oxidising atmosphere.
16. A method according to claim 15, wherein all of the annealing steps are carried out under the selectively oxidising atmosphere.
17. A method according to claim 15, wherein one or more of the annealing steps preceding the final annealing step is carried out under a reducing atmosphere.
18. A method according to any preceding claim, wherein the alloy further comprises a grain refiner.

19. A method according to any one of claims 1 to 18, wherein the alloy is a ternary alloy of silver, copper and germanium.
20. A method according to claim 19 wherein the ternary alloy consists, apart from  
5 impurities and any grain refiner, of 80 to 96% silver, 0.1 to 5% germanium and 1 to 19.9% copper, by weight of the alloy.
21. A method according to claim 19 wherein the ternary alloy consists, apart from  
10 impurities and grain refiner, of 92.5 to 98% silver, 0.3 to 3% germanium, and 1 to 7.2% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.
22. A method according to claim 19 wherein the ternary alloy consists, apart from  
15 impurities and grain refiner, of 92.5 to 96% silver, 0.5 to 2% germanium, and 1 to 7% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.
23. A method according to any one of claims 1 to 18, wherein the alloy is a quaternary alloy of silver, copper, zinc and germanium.
24. A method according to claim 23 wherein the zinc which is present in a ratio, by  
20 weight, to the copper of no more than 1 : 1.
25. A method according to any preceding claim, further comprising producing a finished or semi-finished article from the annealed alloy.
- 25 26. A method according to claim 25, further comprising heat treating the finished or semi-finished article under an air or steam atmosphere at a temperature in the range from 50°C to 200°C for a period in the range from 1 minute to 24 hours to enhance the tarnish resistance of the article.
- 30 27. A method according to any preceding claim, further comprising producing a coin, medal, article of jewellery, holloware or cutlery item from the alloy.

28. An alloy produced by a method according to any of claims 1 to 24.

29. A finished or semi-finished article produced by a method according to any of claims 25 to 27.



(a)

(b)

(c)

Figure 1

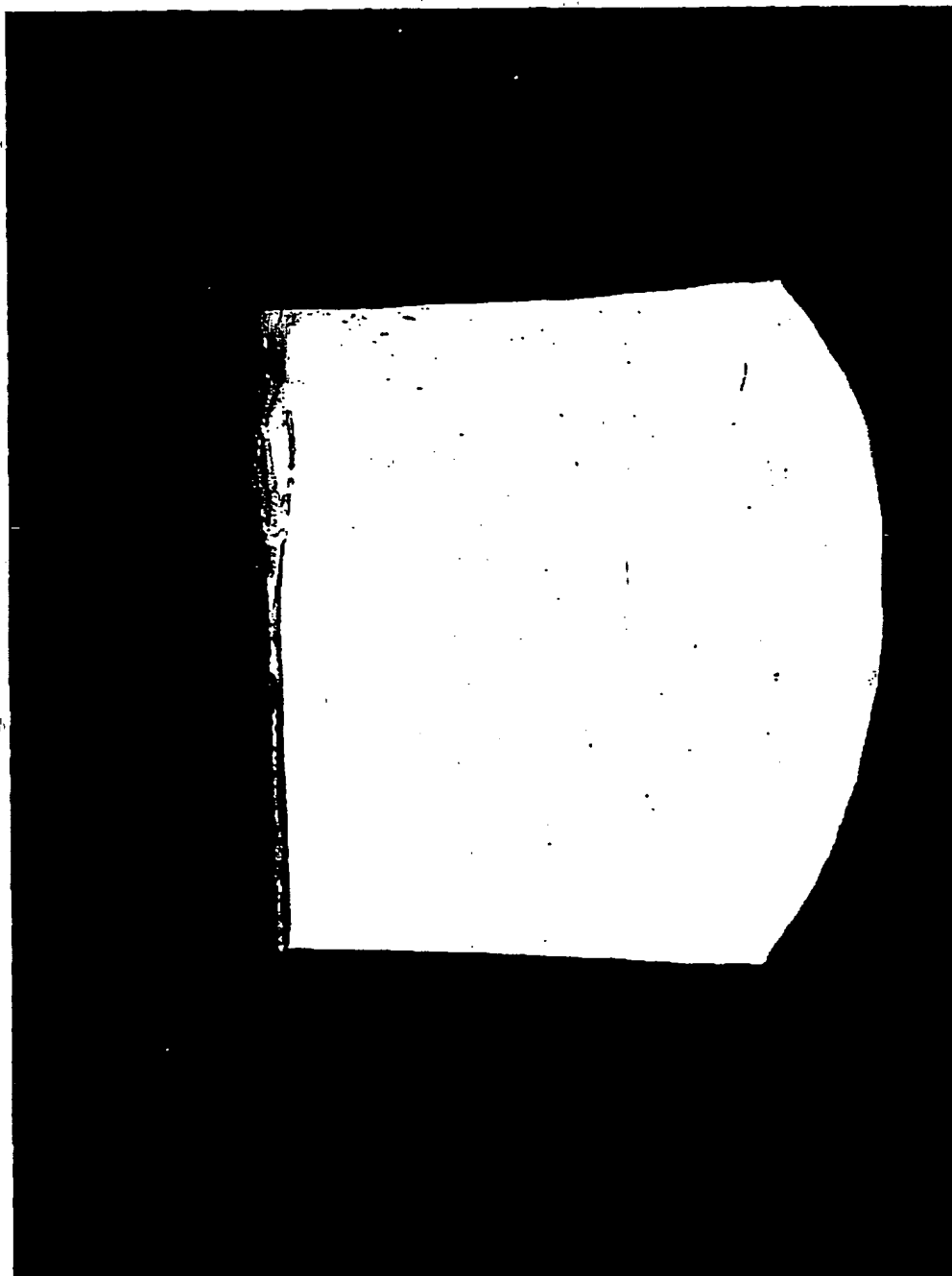


Figure 2

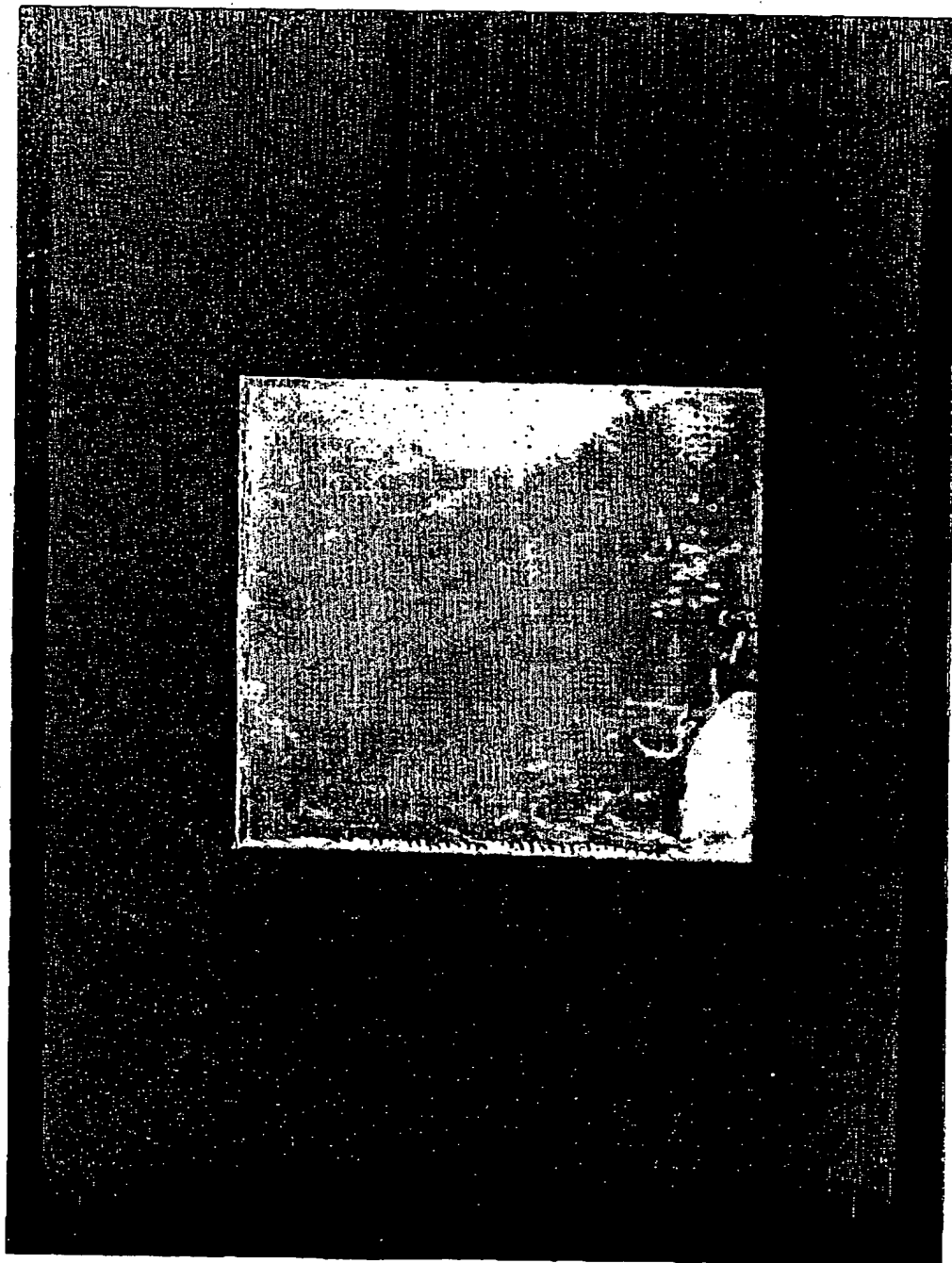


Figure 3



4 / 4

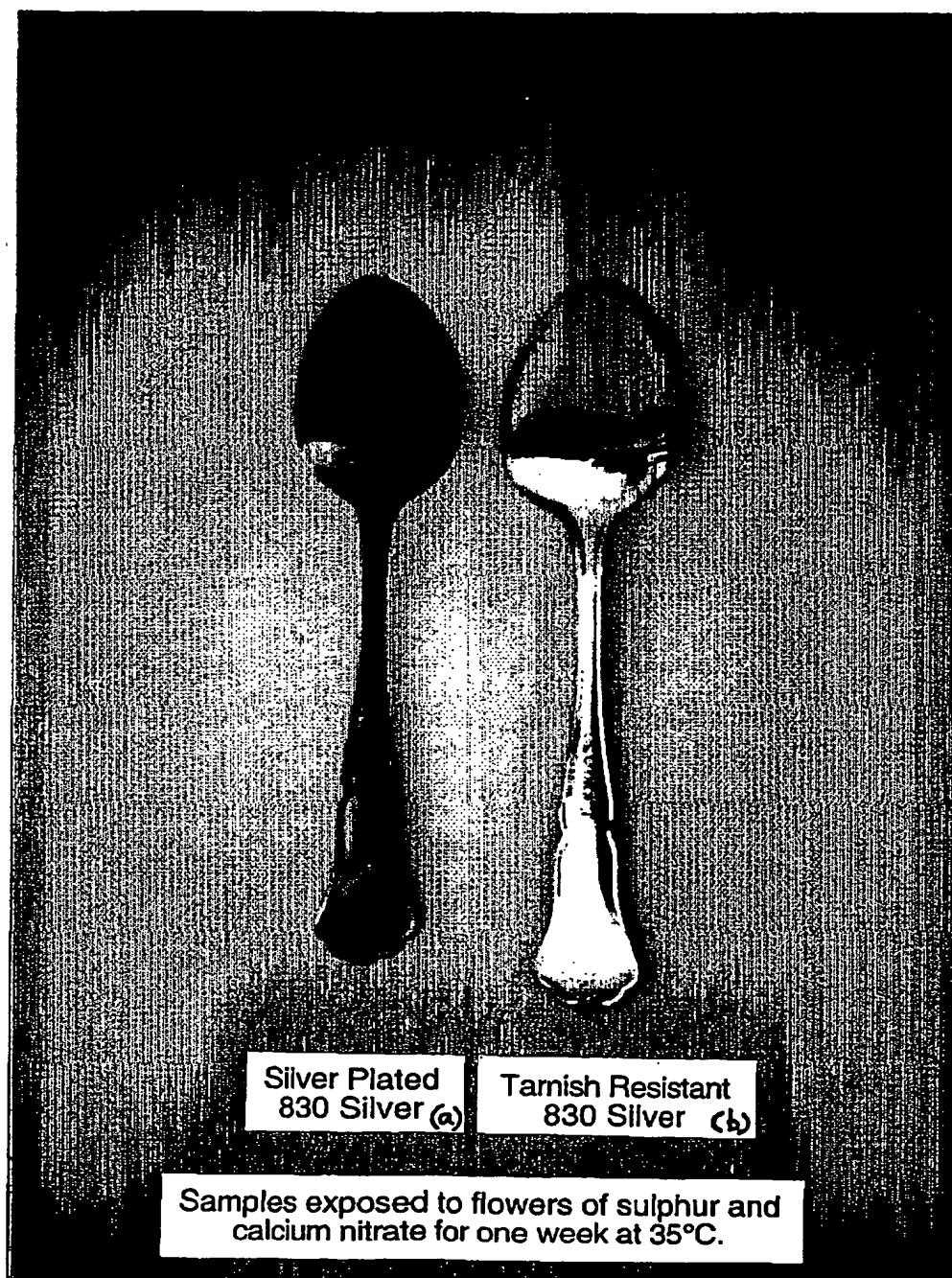


Figure 4